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Organopalladium Approaches to Prostaglandins. 7.[1] Synthesis of Prostaglandin Endoperoxide Analogs by Vinylpalladation of Norbornene

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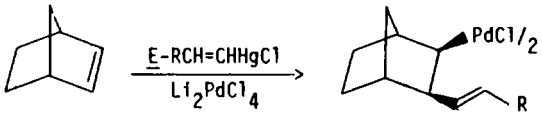
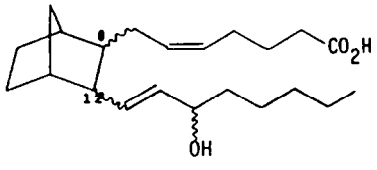
Abstract - Vinylpalladation of norbornene using vinylmercurial **5** and Li_2PdCl_4 affords the corresponding cis-exo adduct **6** which can be directly carbonylated to methyl ester **7** in 60% overall yield. Reduction to aldehyde **9** and subsequent chain elaboration provides the new prostaglandin endoperoxide analog **12**. Epimerization of exo aldehyde **9** to endo aldehyde **13** and chain extension provides the first synthesis of optically active endoperoxide analog **15**, a known potent inhibitor of PGE_2 synthesis. Biological test results for compounds **12** and **15** are reported.

The synthesis of stable analogs of the prostaglandin endoperoxides has received considerable attention in recent years.[2,3] The most common routes to these compounds have involved either modification of naturally occuring prostaglandins or Diels-Alder approaches. Our interest in this area has lead to a number of new approaches involving π-allylic,[4] benzylic,[1,5] and thienyl[6,7] palladium compounds, as well as oxypalladation.[8] Recently, we reported that the facile addition of vinylic palladium species to bicyclic alkenes affords the corresponding stable, cis-exo adducts (eq 1).[9,10] The substantial biological activity of the known endoperoxide analogs **1** (prepared

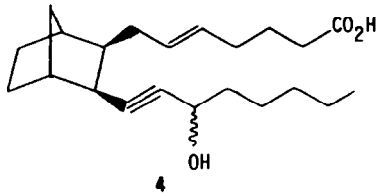


(1)

previously as a racemic mixture of C-15 epimers[11] or a diastereomeric mixture of the two 15-S alcohols[12]) and **2** (prepared previously as a racemic mixture of C-15 epimers[13]), as well as our own cis-exo compound **4** (prepared previously as a racemic mixture of C-15 epimers[4]), encouraged us to examine this reaction as a possible new approach to prostaglandin endoperoxide analogs, particularly compound **1** (as a pair of 15-S diastereomers), and the unknown optically active 15-S stereoisomer **3** (as a pair of diastereomers). We report here the successful conclusion of those studies.



1, 8-endo, 12-exo
2, 8-exo, 12-endo
3, 8-exo, 12-exo



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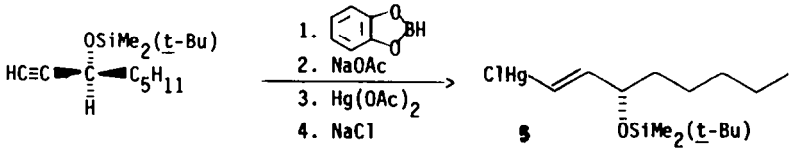
Results and Discussion

The requisite vinylmercurial **5** for our synthesis of compounds **1** and **3** is readily available from optically pure (S)-3-(t-butyldimethylsilyloxy)-1-octyne[1] using our recently improved hydroboration-mercuration procedure[14] (eq 2).



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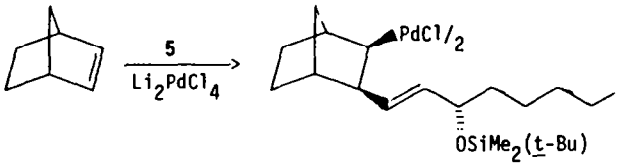
(2)

Vinylpalladation[9,10] of norbornene (10 equiv) using organomercurial **5** afforded the stable adduct **6** in 78% isolated yield (eq 3). This palladium compound is no doubt a mixture of two



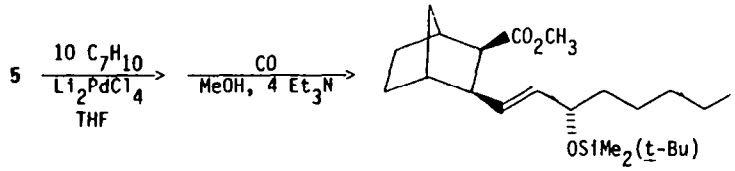
(3)

6

diastereomers resulting from addition of the vinylpalladium species to opposite ends of the carbon-carbon double bond. This is seen from the extra peaks observed in the ^{13}C NMR spectra of the products of subsequent reactions. All subsequent reactions are assumed to contain the analogous pair of diastereomers, though they have not been drawn and could never be separated.

Numerous unsuccessful attempts have been made on a model system to elaborate this type of organopalladium complex to the desired 2-carbon homologated aldehyde **10** in a minimum of steps. Those efforts involved reactions with $ClHgCH_2CHO$, $LiCH_2CN$, $CuCH_2CN$, $LiCH_2CO_2$-*t*-Bu, $LiC{\equiv}COEt$, $LiC{\equiv}CH$, $NaCH(CO_2Et)_2$, *Z*-*n*-$Bu_3SnCH{=}CHOEt$, *Z*-$LiCH{=}CHOEt$, *E*-$Cp_2ZrClCH{=}CHOEt$ and *E*-*o*-$(C_6H_4O_2)BCH{=}CHOEt$ in the presence or absence of triphenylphosphine. Few of these reactions showed any of the desired cross-coupled product. When reaction did occur, it was usually that of substitution of PdCl by hydrogen.

It was subsequently decided that direct carbonylation of this intermediate affords the most efficient method to achieve the desired objective. Thus, vinylpalladation and subsequent carbonylation using 1 atm CO, MeOH and Et_3N (4 equiv) from -78°C to room temperature afforded the corresponding methyl ester **7** in 60% overall yield from mercurial **5** (eq 4).



(4)

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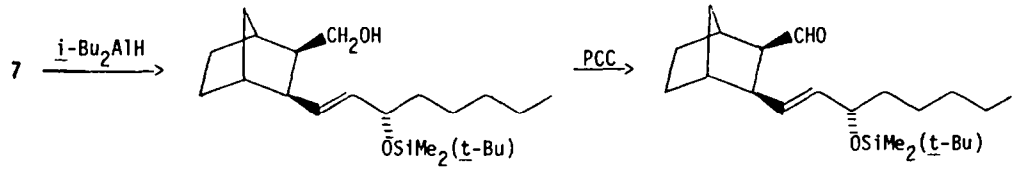
This ester was readily reduced to the corresponding primary alcohol **8** (89% yield) using *i*-Bu_2AlH and reoxidized to the desired aldehyde **9** (95% yield) using pyridinium chlorochromate (PCC) (eq 5).[15] This three-step sequence from palladium complex **6** to aldehyde **9** could be shortened

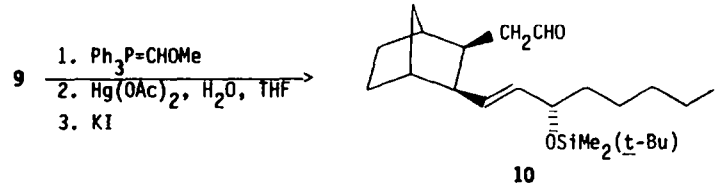


(5)

8 **9**

considerably by treating compound **6** sequentially with CO, PPh_3 (2 equiv) and *n*-Bu_3SnH (1.2 equiv) in one reaction vessel.[7] Unfortunately, the 95% yield of aldehyde **9** obtained the first time using this procedure did not prove reproducible for reasons we do not understand.

Aldehyde **9** was homologated via Wittig olefination[15] and mercuric acetate-promoted hydrolysis of the resulting vinyl ether (eq 6). The yield of aldehyde **10** of only 40% was not optimized and



(6)

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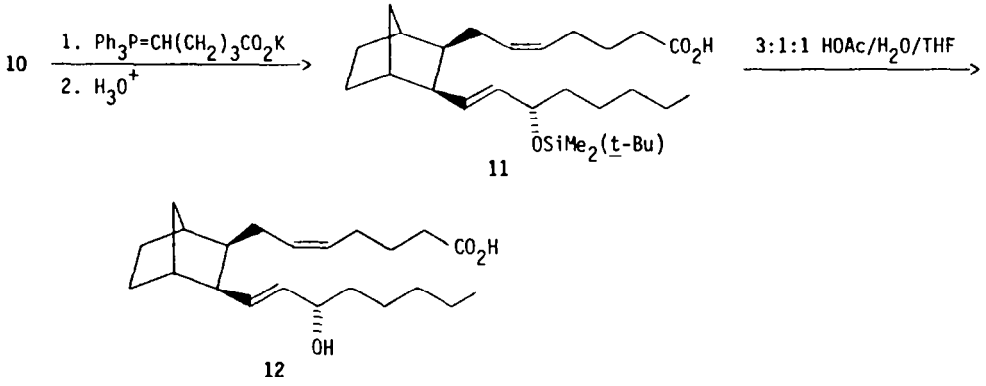
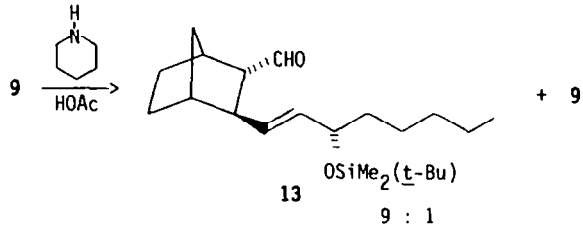
some difficulties were encountered in selectively hydrolyzing the vinyl ether without touching the silyloxy group. Partial hydrolysis of the silyloxy group was observed using 3:1:1 HOAc/THF/H_2O.

Finally, further Wittig olefination[16] and subsequent deprotection of the silyloxy group proceeded in yields of 69% and 84% respectively to afford carboxylic acid 12 (eq 7).



(7)

The aldehyde 9 has proven to be a valuable intermediate for not only the synthesis of the cis-exo acid 12, but it allows easy entry into the C-8 endo, C-12 exo systems, as illustrated by the following synthesis of the known[11,12] endoperoxide analog 15 prepared here for the first time in optically active form as a pair of diastereomers. Aldehyde 9 was epimerized[17] to a 9:1 mixture of compounds 13 and 9 using piperidine and acetic acid in refluxing benzene (eq 8). Aldehyde 13 was carried on to carboxylic acid 15 using an identical sequence to that described above (eq 9). Attempts to separate these diastereomers by HPLC have so far proven unsuccessful. It appears that only diastereomers epimeric at the C-15 alcohol are easily separable.



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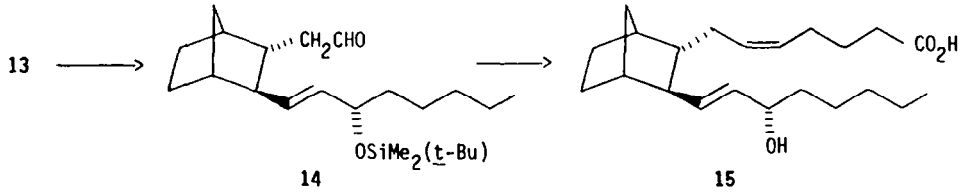

(9)

The biological testing of compounds 12 and 15 was carried out by E. R. Squibb and Sons, Inc. For acid 12 the effective concentration (I_{50}) for 50% inhibition of arachidonic acid (AA)-induced blood platelet aggregation was 8.25 μM, while the figure for ADP-induced aggregation was 1,394 μM. The corresponding figures for compound 15 were 9.46 μM and 407 μM. Note the greater selectivity (AA over ADP) of the cis-exo compound 12. A racemic mixture of C-15 epimers of compound 15 has previously been shown to be a potent inhibitor of PGE_2 synthesis.[11]

Experimental Section

Reagents. All chemicals were used as obtained commercially unless noted otherwise. All solvents were distilled before use. The following chemicals were obtained from Aldrich: norbornene, 1-octyn-3-ol, diisobutylaluminum hydride (1 M solution in hexane), pyridinium

chlorochromate, methoxymethyltriphenylphosphonium chloride, potassium t-butoxide, (4-carboxybutyl)triphenylphosphonium bromide.

Equipment. ^{1}H and ^{13}C NMR spectra were recorded on a Nicolet-300 MHz NMR spectrometer. IR spectra were recorded on a Beckman-4250 spectrometer. Exact mass analyses were performed on a high resolution MS-50 mass spectrometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee. Biological testing was done by E. R. Squibb and Sons, Inc., Princeton, New Jersey.

Synthesis of organomercurial 5. Organomercurial 5 was prepared from optically pure (S)-3-t-butyldimethylsilyloxy-1-octyne[1] using our recently published procedure for the racemic material.[14]

Synthesis of ester 7 from vinylmercurial 5. A solution of dilithium tetrachloropalladate (3.6 mmol) and norbornene (3.38 g, 36 mmol) in 54 ml of tetrahydrofuran (THF) was cooled to 0°C under a nitrogen atmosphere. (E)-3-(t-butyldimethylsilyloxy)-1-(chloromercurio)-1-octene (5) (1.717 g, 3.6 mmol) dissolved in 18 ml of THF was added, and the reaction mixture was allowed to slowly warm to room temperature and stirred overnight. Then the reaction mixture was diluted with methylene chloride, filtered through Celite to remove palladium black, washed with aqueous NH_4Cl and water, and dried over anhydrous $MgSO_4$. The solvent was removed under vacuum to provide the crude organopalladium compound **6**.

To a stirred solution of 1.66 g (3.49 mmol) of the crude organopalladium compound **6** in 65 ml of 4:1 methanol/THF, cooled to -78°C, was added triethylamine (2.0 ml, 14.4 mmol). After flushing the reaction flask with carbon monoxide, a balloon of carbon monoxide was placed on the reaction flask and the reaction mixture was allowed to slowly warm to room temperature and stirred overnight. The solution was diluted with ether; filtered through Celite to remove palladium black; washed with dilute HCl, aqueous $NaHCO_3$ and water; and then dried over anhydrous Na_2SO_4. The solvent was removed under vacuum to afford an oil which was purified using flash column chromatography with 19:1 hexane/ethyl acetate giving 0.85 g (60% overall) of ester 7: ^{1}H NMR ($DCCl_3$) δ 0.0 (6 H, s, $SiMe_2$), 0.85-2.5 (30 H, m, t-Bu, C_5H_{11} and norbornyl), 3.57 (3 H, s, OCH_3), 4.00 (1 H, m, C=CCHO-), 5.45 (2 H, m, vinyl); IR (neat) 2980, 2945, 2900, 2880, 1745, 1610 (w), 1370, 1250 cm^{-1}; ^{13}C NMR ($DCCl_3$) (300 MHz) δ -4.61, -4.21, 14.12, 18.26, 22.69, 24.97, 25.95, 28.85, 28.99, 31.91, 35.37, 38.53, 39.82, 39.98, 42.24, 42.89, 49.91, 51.01, 55.79, 72.72, 73.85, 129.28, 130.09, 134.78, 135.16, 174.09; mass spectrum, m/e 323.20477 [calcd for $C_{18}H_{31}O_3Si$ (M^+-C_5H_{11}), 323.20425].

Synthesis of alcohol 8. Alcohol **8** was prepared using a procedure similar to one reported earlier.[15] To a stirred solution of the ester 7 (1.18 g, 2.99 mmol) in 30 ml of dry diethyl ether, cooled in a dry ice bath to -78°C under an atmosphere of nitrogen was slowly added 7.5 ml of 1M diisobutylaluminum hydride in hexane. The reaction mixture was stirred at -78°C for 4 h and then quenched with 3 ml of cold methanol. It was then cautiously poured into a mixture of 50 g of ice, 1.5 ml of conc H_2SO_4 and 50 ml of hexane with stirring. The aqueous layer was separated and extracted with hexane. The combined hexane extracts were washed with saturated aqueous sodium chloride solution and water, and dried over anhydrous sodium sulfate. The solvent was removed under vacuum to give 0.97 g (89%) of alcohol **8**: ^{1}H NMR ($DCCl_3$) (300 MHz) δ 0.0 (6 H, 2 s, $SiMe_2$), 0.80-2.3 (30 H, m, t-Bu, C_5H_{11} and norbornyl), 3.25-3.6 (2 H, m, $-CH_2O-$), 4.0 (1 H, m, C=CCHO-), 5.4-5.5 (2 H, m, vinyl); IR (neat) 3300, 2940, 2920, 2860, 2840, 1450, 1240, 820, 760 cm^{-1}; ^{13}C NMR (300 MHz) δ -4.68, -4.28, 14.07, 16.27, 22.68, 25.07, 25.94, 29.00, 29.88, 31.86, 38.69, 38.54, 38.80, 43.09, 43.43, 48.39, 48.47, 49.90, 63.96, 65.86, 73.02, 73.46, 130.05, 130.22, 134.80, 134.98; mass spectrum, m/e 309.22467 [calcd for $C_{18}H_{33}O_2Si$ (M^+-57), 309.22499].

Synthesis of aldehyde 9. Aldehyde **9** was prepared by a procedure analogous to one reported earlier.[15] Pyridinium chlorochromate (1.84 g, 3.89 mmol) was suspended in CH_2Cl_2 (5.2 ml), and the alcohol **8** (0.95 g, 2.60 mmol) in 4.5 ml of CH_2Cl_2 was rapidly added at room temperature. The solution became briefly homogeneous before depositing the black, insoluble, reduced reagent. After 1 h the black mixture was diluted with 5 volumes of ether, the solvent was decanted, and the

black solid was washed twice with ether. The product **9** was isolated simply by filtration of the organic extracts through a Florisil column and evaporation of the solvent at reduced pressure: 0.899 g, 95% yield; ^{1}H NMR ($DCCl_3$) δ 0.0 (6 H, 2 s, $SiMe_2$), 0.83-2.83 (30 H, m, t-Bu, C_5H_{11} and norbornyl), 4.0 (1 H, m, C=CCHO-), 5.39-5.7 (2 H, m, vinyl), 9.60 (1 H, m, CHO); IR (neat) 2940, 2920, 2840, 2700, 1715, 1450, 1245, 960, 820, 710 cm^{-1}; ^{13}C NMR (300 MHz) ($DCCl_3$) δ -4.74, -4.33, 13.98, 18.19, 22.60, 24.89, 25.87, 28.52, 29.09, 31.79, 34.95, 37.09, 37.15, 38.38, 42.71, 42.98, 48.85, 48.99, 59.07, 72.98, 73.30, 128.88, 129.05, 135.25, 135.41, 203.68; mass spectrum, m/e 307.20906 [calcd for $C_{18}H_{30}O_2Si$ (M^+-57), 307.20934].

Synthesis of aldehyde **10**. Aldehyde **10** was synthesized using a procedure analogous to one reported previously.[15] Lithium diisopropylamide (0.81 mmol in 0.86 ml of THF) was added to methoxymethyltriphenylphosphonium chloride (0.343 g, 0.86 mmol) in toluene (3.1 ml) at 0°C and stirred for 10 min. The aldehyde **9** (0.196 g, 0.54 mmol) in 1 ml 3.4:1 toluene/THF was added to the bright red ylide at 0°C and stirred for 1 h. The reaction mixture was diluted with ether and then washed with brine and water, and dried over anhydrous $MgSO_4$. The solvent was removed and the residue was dissolved in 5 ml 10:1 THF/H_2O. Mercuric acetate (0.48 g, 1.5 mmol) was added and the reaction mixture was stirred for 5 min at room temperature. Saturated potassium iodide solution (10 ml) was added and the reaction mixture was extracted with ether. The combined ether layers were washed with brine and water and dried over $MgSO_4$. The solvent was removed on a rotary evaporator and the residue was purified by flash chromatography using 9:1 hexane/ethyl acetate to give 81 mg of aldehyde **10**: 40% overall yield from aldehyde **9**; ^{1}H NMR ($DCCl_3$) (300 MHz) δ 0.0 (6 H, 2 s, $SiMe_2$), 0.8-1.0 (12 H, t-Bu and CH_3), 1.0-2.5 (20 H, m, norbornyl and methylenes), 4.0 (1 H, m, C=CCHO-), 5.20-5.40 (2 H, m, vinyl), 9.67 (1 H, m, CHO); IR (neat) 2920, 2860, 2840, 2700, 1720, 1450, 1240, 960 cm^{-1}; ^{13}C NMR ($DCCl_3$) (300 MHz) δ -4.72, -4.63, -4.30, -4.14, 13.95, 18.19, 22.61, 24.87, 24.97, 25.90, 28.93, 28.97, 29.76, 31.83, 33.23, 33.28, 38.46, 38.58, 41.02, 41.55, 42.95, 43.22, 46.37, 49.00, 49.11, 72.96, 73.47, 130.15, 130.50, 134.84, 135.12, 201.82; mass spectrum, m/e 377.28748 [calcd for $C_{23}H_{41}O_2Si$ (M^+-H), 377.28759].

Synthesis of acid **11**. Acid **11** was prepared according to a previously published procedure.[16] Potassium t-butoxide (0.833 g, 7.4 mmol) was slowly added with stirring to a dry THF (14 ml) suspension of (4-carboxybutyl)triphenylphosphonium bromide (1.61 g, 3.7 mmol) under an atmosphere of nitrogen at room temperature. The deep red solution was then stirred for 15 min. To this was slowly added aldehyde **10** (0.353 g, 0.93 mmol) in dry THF (9 ml). The solution turned chocolate brown and was stirred for 3 h. Water (50 ml) and 2N H_2SO_4 (40 ml) were then added. Extraction with diethyl ether gave an organic fraction which was again washed with 2N H_2SO_4 (2 x 20 ml) and water (3 x 20 ml) and dried. Purification by column chromatography using 1:1 hexane/ethyl acetate gave 300 mg (69%) of compound **11**: ^{1}H NMR ($DCCl_3$) δ 0.0 (6 H, 2 s, $SiMe_2$), 0.70-0.93 (12 H, t-Bu and CH_3), 1.06-2.39 (26 H, m, norbornyl and methylenes), 3.91-4.05 (1 H, m, C=CCHO-), 5.18-5.47 (4 H, m, vinyl), 9.4 (1 H, br s, CO_2H); IR ($DCCl_3$) 3400-2400 (OH), 2965, 2940, 2880, 2860, 1720, 1260, 970 cm^{-1}; mass spectrum, m/e 462.35221 (calcd for $C_{28}H_{50}O_3Si$, 462.35293).

Synthesis of hydroxy acid **12**. Compound **11** (160 mg, 0.346 mmol) was dissolved in 3:1:1 acetic acid/THF/H_2O mixture (6.92 ml) and stirred at room temperature for 30 h. The solvents were evaporated. The residue was taken up in ether and washed with water, dried over magnesium sulfate and concentrated. Column chromatography using 1:1 hexane/ethyl acetate plus a few drops of acetic acid gave 101 mg (84%) of compound **12**: ^{1}H NMR ($DCCl_3$) δ 0.73-1.0 (3 H, m, CH_3), 1.0-2.47 (26 H, m, norbornyl and methylenes), 4.0-4.2 (1 H, m, C=CCHO-), 5.24-5.67 (4 H, m, vinyl), 6.6-7.2 (2 H, broad s, OH and CO_2H); ^{13}C NMR ($DCCl_3$) (300 MHz) δ 13.99, 22.62, 24.51, 24.58, 25.15, 26.44, 26.57, 29.05, 29.24, 29.32, 29.97, 31.81, 32.76, 33.07, 37.27, 40.04, 40.13, 42.99, 43.40, 47.51, 47.74, 49.45, 49.81, 73.22, 73.60, 128.35, 131.67, 131.78, 132.45, 132.53, 133.19, 133.84, 179.07; mass spectrum, m/e 330.2563 [calcd for $C_{22}H_{34}O_2$ (M^+-H_2O), 330.2558]. Anal. Calcd for $C_{22}H_{36}O_3$: C, 75.86; H, 10.34. Found: C, 75.66; H, 10.17.

Synthesis of aldehyde **13**. The following variation of a literature procedure[17] was employed. To a benzene solution of aldehyde **9** (0.55 g, 1.51 mmol in 5 ml) was added 0.17 ml of

acetic acid and 0.17 ml of piperidine. The reaction mixture was refluxed for 3 h. The reaction mixture was cooled, poured into ice water, and extracted with benzene. The benzene layer was washed with dilute HCl, saturated $NaHCO_3$ and brine, and dried over $MgSO_4$. The solvent was evaporated to give 0.44 g (80%) of aldehyde **13** along with aldehyde **9** in a ratio of ~9:1 as seen by ^1H NMR spectral analysis. The endo aldehyde exhibits a peak at δ 9.75 and the exo aldehydic proton appears at δ 9.60.

Synthesis of aldehyde **14**. Compound **14** was synthesized using the same sequence as for compound **9** using the 9:1 mixture of aldehydes **13** and **9**. Compound **14** was separated from the corresponding exo aldehyde by column chromatography using 9:1 hexane/ethyl acetate: 25% unoptimized yield; ^1H NMR ($DCCl_3$) δ 0.0 (6 H, 2 s, $SiMe_2$), 0.8-1.0 (12 H, s and m, t-Bu and CH_3), 1.2-2.6 (20 H, m, norbornyl and methylenes), 4.0 (1 H, m, C=CCHO-), 5.35-5.55 (2 H, m, vinyl), 9.70 (1 H, m, CHO); ^{13}C NMR ($DCCl_3$) δ -4.89, 13.80, 18.04, 21.90, 21.95, 22.41, 24.84, 25.71, 29.71, 31.57, 37.09, 38.27, 40.04, 40.17, 42.20, 42.72, 42.94, 45.73, 45.86, 51.71, 73.30, 73.37, 132.13, 133.10, 133.16, 201.97; mass spectrum, m/e 321.2247 [calcd for $C_{19}H_{33}O_2Si$ (M^+-C_4H_9), 321.2249].

Synthesis of acid **15**. Compound **15** was synthesized by the same reaction sequence as used for compound **12**: ^1H NMR ($DCCl_3$) δ 0.83-2.50 (29 H; m; norbornyl, methylene sidechain and methyl protons), 4.00-4.20 (1 H, m, C=CCHO-), 5.20-5.65 (4 H, m, vinyl), 6.0-7.0 (2 H, br s, OH and CO_2H); ^{13}C NMR ($DCCl_3$) δ 14.00, 22.04, 22.63, 24.71, 25.15, 26.53, 26.57, 28.70, 29.03, 29.17, 29.35, 29.71, 29.99, 30.16, 31.80, 33.17, 33.36, 37.31, 37.58, 39.55, 39.89, 40.03, 43.04, 48.71, 49.17, 52.20, 52.49, 73.21, 73.53, 128.43, 129.64, 130.03, 130.11, 130.27, 136.53, 137.10, 178.43; IR (neat) 3600-2500, 3300, 3040, 2960, 2940, 2880, 1720, 1470, 970, 760 cm^{-1}; mass spectrum, m/e 348.26564 (calcd for $C_{22}H_{36}O_3$, 348.26645). Anal. Calcd for $C_{22}H_{36}O_3$: C, 75.86; H, 10.34. Found: C, 73.99; H, 10.41.

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References and Notes

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